

## Reactive Oligomer to Improve the Impact Characteristics of Structural Composites Used in Civil and Medical Applications

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**Abstract:** Composite materials are increasingly utilized in many civil engineering and medical applications such as conveying tubes and pipelines, making artificial human parts, dental applications, reinforcing structures, etc. The glass reinforced composite is one of the most common composite that is used for its good mechanical properties and also its rationally low price. Polymeric resins such as epoxy are used as the constitutive material in producing glass reinforced composites. In this research paper we improve the impact resistance of the glass-reinforced composite using Hycar reactive oligomer. Mechanical impact strength tests have been conducted using a notched sample. The obtained test results show that the impact resistance of Hycar modified glass-reinforced composite is enhanced by addition of the Hycar to the glass reinforced composite. Moreover the glass transition temperature ( $T_g$ ) of the samples has been measured experimentally using a differential scanning calorimeter (DSC) instrument. The results of measuring  $T_g$  however shows that these improvements in impact resistance of the composite material are accompanied with a slight reduction in the glass transition temperature of the modified composite samples. Moreover the damaged surfaces of fractured samples were investigated using scanning electron microscopy (SEM) techniques.

**Key words:** Glass reinforced composite • Hycar modifier • Impact properties • Glass transition temperature

### INTRODUCTION

Polymers and composites becomes the center of interest in engineering, manufacturing, medicines and other branches of applied sciences [1-7]. In recent decades glass reinforced composites are frequently used in reinforcing old structures, bridges and other applications. Moreover these materials are highly used in making prostheses, dental applications, fabrication of human parts and other medical applications. But, composite materials suffer from a mechanical weakness that restricts its application in many structural applications: They are rationally brittle and exhibit a low impact resistance [8-10]. Please note that for a leg prostheses or for a bridge structure that make from composite materials, many impact loading might be occurred during its operational life. This implies the

importance of high impact strength of composite materials for high performance applications. Addition of secondary polymeric phase to a polymer matrix is an appropriate method for improving impact resistance of these composites [11-14]. Other methods of improvement might not be as effective as addition of rubber to the composites. Liquid rubbers might be utilized as modifiers for this purpose [14]. The rubber modification of composites has been studied in previous publications. For example, Ophir *et al.* [15] investigated a modified glass reinforced composite for producing pressure vessels. Moreover, Zhang *et al.* [16] used CTBN to modify the toughness of composite pipes. Another study showed negligible increase in impact strength of composites which was the result of low toughenability of the resin used [17]. Abadyan *et al.* [18] observed that addition of amine-terminated butadiene acrylonitrile (ATBN) to epoxy

matrix increases impact strength of modified hoop wound composite but reduces its compressive and interlaminar shear strength. Moreover incorporation of ATBN led to more favorable mechanical properties, from the viewpoint of both toughness and strength, relative to CTBN [19]. Sobrinho *et al.* [20, 21] applied a CTBN-modified epoxy system for development of composite pipes for riser application in deep water. The influence of matrix toughening and the number of composite layers on the mechanical behavior of the tubes were investigated by hydrostatic and split-disk tests [20, 21]. Moreover, exploring the energy absorption of hybrid modified epoxies containing soft particles has been accomplished in [22]. They observed that addition of 3<sup>rd</sup> polymeric phase (coarse waste tire particles) to a modified epoxy (bi-modal epoxy) might reduce the energy absorption of the composite. In Ref. [23] it has been demonstrated that the enhancing the loading rate of modified epoxy samples might lead to reduce the energy absorption of samples. It means that composite materials that are high energy absorption capability in static loading might be brittle in impact dynamic loading. This reference shows that cavitation has a great influence on the fracture toughness of epoxy matrix. Moreover, the incorporation of two types of rubber modifier on toughness and energy absorption of bi-modal composite epoxy has been examined [24-25]. The researchers reported a synergistic toughening in epoxy modified by a combination of two modifier particles [24-25]. However it has been claimed that this synergism might not be useful for dynamic loading since this is very sensitive to the high loading rate. This means one cannot use a bi-modal epoxy for fabrication of structural composites that might be subjected to impact loadings.

Despite the studies done on rubber-modified epoxy composites, there is still lack of knowledge on the role of modifier particles in the overall performance of wound composites. Only few works has been focused systematically on investigation of the impact resistance of composite materials. Therefore, the goal of the current investigation is to study the role of rubber modification in

performance of hoop wound tubes in a more systematic fashion. A Hycar 1300×16 oligomer is used to modify the epoxy matrix and the corresponding wound composites. In order to do a systematic study, the influences of modifiers on the epoxy matrix are investigated first. Physical evaluations are incorporated as well as microscopy.

## MATERIALS AND METHOD

The typical resin system used in this work for fabrication of composite samples is diglycidyle ether of bisphenol A epoxy resin (trade name of Araldite LY5052) and a polyamine hardener (trade name of HY5052). In order to fabricate glass-reinforced samples, glass fiber roving has been used for filament winding the test samples. Reinforcement used was a glass rowing with 2400 tex from Vetrotex. The reactive oligomer modifier is used was the Hycar 1300×16 with 16 wt% of acrylonitrile, from Novion company.

**Sample Preparation:** In order to make the samples, the stoichiometric ratio of the curing agent and resin were cured for 8h at 80°C. The modifier content (Hycar content) was varied from 0 up to 20 phr. We added the Hycar modifier before adding the hardener agent. After preparing the resin samples, we fabricated the filament wound composite samples. All formulations were reinforced with glass fiber. First resin has been modified with Hycar material and then the compound has been glass reinforced in the machine resin bath before applying on the mandrel. For this purpose we used a 3-degree of freedom (3-DOF) filament wound automatic machine. After that, we cured the samples according to the datasheet instruction above. The composite formulation used is listed in Table 1.

**Characterization Techniques:** In order to evaluate the behavior of Hycar modified samples, we have used two techniques including measuring the impact resistance and glass transition temperature of the wound samples.

Table 1: Resin formulations made in this study

Sample code	Resin (phr)	Hardener (phr)	Modifier type	Modifier Content (phr)
NC	100	38	-	0
CV5	100	38	Hycar1300×16	5
CV10	100	38	Hycar1300×16	10
CV15	100	38	Hycar1300×16	15
CV20	100	38	Hycar1300×16	20

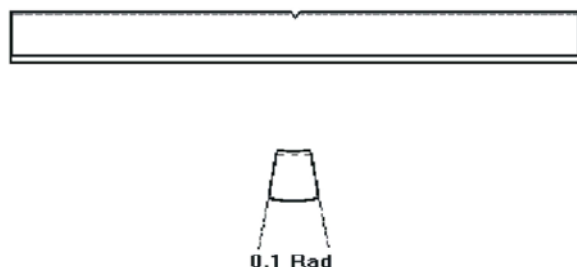


Fig. 1: Schematic diagrams of geometries used for impact test.

**Impact Resistance:** A Charpy impact test (B method) was accomplished according to ASTM D256 using standard notched specimens. Samples were prepared by casting and machined to the standard shape. Tests were performed with a 1-J hammer. Since there is not any specific test for wound composites, similar to this standard we applied a test method previously has been used by other researchers. The composite impact resistance is measured using an un-notched test sample. Impact specimens were cut from 90 mm inner diameter composite cylinders according to Figure 1. Notch geometry was similar to that mentioned in ASTM D256. Each reported value is the average result of five independent specimens.

**Glass Transition Temperature:** Glass transition temperature is an important parameter for evaluating the temperature-dependent mechanical characteristics of a material. This is very essential for structural designers since this parameter shows the performance and durability of the structural composite in a high operational temperature. The glass transition temperatures ( $T_g$ ) of the composite were determined by a differential scanning calorimeter DSC equipment. The samples were heated from 70 to 120°C at the heating rate of 10°C/min.

**Microscopy Evaluation:** The surfaces of the specimens were examined using scanning electron microscope (SEM). In order to produce a conductive surface the fractured surface of samples were first coated with a thin layer of gold. After that, the surface has been investigated under a high electrical voltage differences.

## RESULTS AND DISCUSSION

**Impact Strength:** The results of impact strength are reported in Table 2. It is observed that the increase in Hycar modifier content led to increased impact strength of composite samples. Considering the volume fraction of

Table 2: Impact strength of composite tubes

Sample	Impact Strength
CN	5.91
CV5	7.11
CV10	7.84
CV15	8.01
CV20	7.19

Table 3: Glass transition temperature of resin

Sample	Tg(C)
N	110
V5	109
V10	109
V15	109
V20	108

fibers in the composite, Hycar content of modified composite is only about 20% of that of the unreinforced material.

In earlier investigation similar type of impact test was used to evaluate impact strength of rubber modified samples [13]. However note that no significant increase in impact strength of the composite is observed. This is because epoxy resin that they used was brittle and therefore to be toughened by Hycar modification. This is why no improvement in impact strength of the composite was observed.

### Glass Transition Temperature ( $T_g$ ) Evaluation:

Glass transition temperature is an important parameter for evaluating the temperature-dependent mechanical characteristics of a material. This is very essential for structural designers since this parameter shows the performance and durability of the structural composite in a high operational temperature. The glass transition temperatures ( $T_g$ ) of the composite were determined by a differential scanning calorimeter DSC equipment.

The glass transition temperature ( $T_g$ ) are listed in Table 3. Decrease in glass transition temperature is reported in samples containing Hycar. Increasing Hycar content leads to a slight decrease in  $T_g$ . The reduction in  $T_g$  of composite by addition of oligomer can be expressed via incomplete precipitation of Hycar from the composite matrix. This topic has been investigated previously by researchers. Incomplete precipitation of Hycar can increase toughness and decrease compressive and flexural strength of modified resin.

**SEM Fractography:** As mentioned before, in order to produce a conductive surface the fractured surface of samples were first coated with a thin layer of gold.

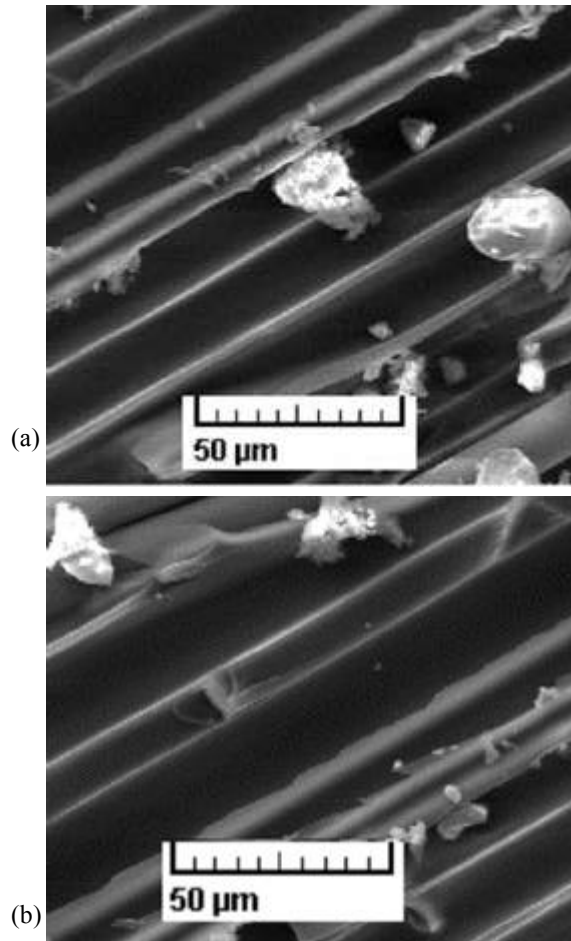


Fig. 2: SEM micrographs of surface of composite impact samples: (a) CN, (b) CV10.

After that, the surface has been investigated under a high electrical voltage differences. In figure 2 we present the SEM images of the fracture surface of impact samples. Rough morphology is observed for unmodified sample. However in the case of modified resin, cavitated rubber particles are observed in the resin surface.

The mechanisms of enhancing impact resistance of composite materials by Hycar can be illustrated in figure 3. First, the solution of liquid oligomers in the epoxy matrix (0) precipitates into two distinct phase of epoxy and Hycar spheres (1) during the curing process. By applying an impact loading on the specimen, the external stress induces during impact (2) which causes the matrix to cavitate (3) and voids nucleate. The size of these cavities increases by increasing the stress during impact (4) and produce a plastic deformation in the matrix. These plastic deformation and holes can pin and arrest the microcracks that occur during the impact loading (5).

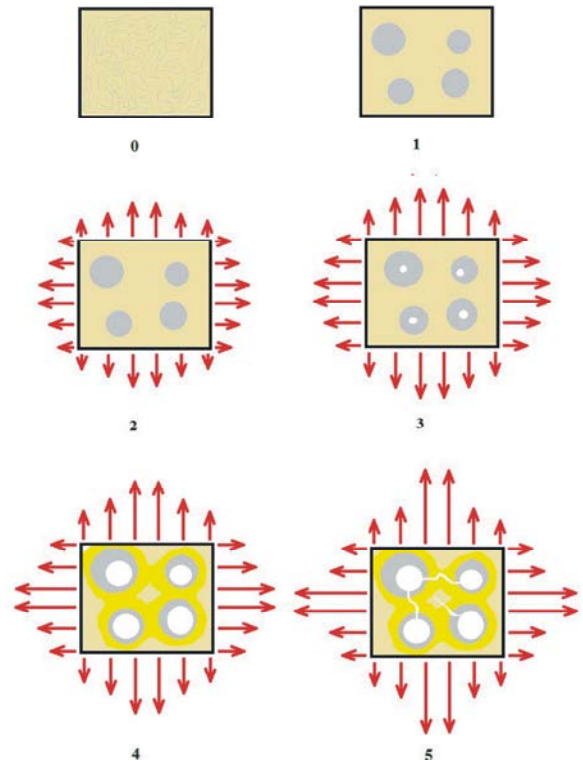


Fig. 3: Mechanisms of Hycar in increasing the impact resistance of composite samples: The solution of liquid oligomers in the epoxy matrix (0) precipitates into two distinct phase of epoxy and Hycar spheres (1). Applying the external stress during impact (2) causes the matrix to cavitate (3). The cavities increase by increasing the stress during impact (4) and they pin the microcracks that occur during the impact loading (5).

## CONCLUSIONS

It is well-established that the epoxy-based glass reinforced composite is one of the most common composite that is used for its good mechanical properties and low price. In this paper Hycar was employed as toughener in glass reinforced composites. Moreover, the SEM fractography has been conducted to better understand the composite behavior. Impact strength and glass transition temperature of composites has been influenced by Hycar modification. The obtained test results show that the impact resistance of Hycar modified glass-reinforced composite is enhanced by addition of the Hycar to the glass reinforced composite. However, the results of measuring  $T_g$  however shows that these improvements in impact resistance of the composite

material are accompanied with a slight reduction in the glass transition temperature of the modified composite samples.

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